CARBON DIHALIDES AS INTERMEDIATES IN THE BASIC HYDROLYSIS OF HALOFORMS

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TABLE OF CONTENTS

LIST OF TABLES

CARBON DIHALIDES AS INTERMEDIATES IN THE BASIC HYDROLYSIS OF HALOFORMS

SUMMARY

Evidence is presented to show that the basic hydrolysis of a number of haloforms proceeds through the intermediate formation of a carbon dihalide. The effect of structure on the relative reactivities of these haloforms is discussed in terms of this mechanism.

INTRODUCTION

This work is a continuation of the study by Hine[1], in which it was shown that the most probable mechanism for the basic hydrolysis of chloroform was through a carbon dichloride intermediate. The present study was initiated to determine whether the same mechanism would explain the basic hydrolysis of some other haloforms. It was also desired to study the effect of structure on the relative reactivities of these haloforms. The haloforms studied were bromoform, chlorodibromomethane, bromodichloromethane, chloroform, and fluorochlorobromomethane. In additon methylene bromide, methylene chlorobromide and carbon tetrabromide were studied to compare their rates of hydrolysis with the haloforms.

Activation energies of the haloform reactions were determined. The carbon dihalide mechanism proposed to explain this reaction of the haloform is:

I. $CHX_3 + OH^- \overset{\text{fast}}{\rightleftharpoons} CX_3^- + H_2O$

$CX_3^- \overset{\text{slow}}{\longrightarrow} CX_2 + X^-$

$CX_2^- \overset{\text{fast}}{\xrightarrow[OH^-,\ H_2O]{}} CO \text{ and } HCO_2^-$

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[1]Jack Hine, J. Am. Chem. Soc., 72, 2438 (1950).

This mechanism is supported by the data on the base catalyzed deuterium exchange of $CHBr_2Cl$ and $CHBrCl_2$[2], which showed that the exchange reaction is rapid compared to the hydrolysis, therefore implying the possibility of the equilibrium in the first step of the mechanism.

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[2] R. H. Sherman and R. B. Bernstein, J. Am. Chem. Soc. 73, 1376 (1951).

DISCUSSION OF THE RESULTS

Mechanism.

The basic hydrolysis of the haloforms studied was found to be second order, first order in hydroxide ion and first order in haloform (Table I). The only exception was found in the case of CHFClBr, where the value constantly decreased. The explanation of this fact is not known.

The most reasonable mechanisms that are consistent with these kinetics are mechanism I (page 2) and mechanisms II and III below.

II. The S_N2 mechanism.

$$CHX_3 + OH^- \xrightarrow{\text{slow}} HOCHX_2 + X^-$$
$$HOCHX_2 \xrightarrow[OH^-,\ H_2O]{\text{fast}} CO \text{ and } HCO_2^-$$

III. An S_N2 attack by H_2O on the CX_3^- anion.

$$CHX_3 + OH^- \overset{\text{fast}}{\rightleftharpoons} H_2O + CX_3^-$$
$$H_2O + CX_3^- \xrightarrow{\text{slow}} H_2\overset{\oplus}{O}\text{-}\overset{\ominus}{C}X_2 + X^-$$
$$H_2\overset{\oplus}{O}\text{-}\overset{\ominus}{C}X_2 \xrightarrow[OH^-,\ H_2O]{\text{fast}} CO \text{ and } HCO_2^-$$

Consideration of the relative reactivities of the halides of methane (Table I) indicates substantial evidence against the S_N2 mechanism for the basic hydrolysis of the haloforms, as it can be easily seen that the haloforms are more reactive than either the methylene halides or the

Table I: Relative Rates of Reaction of Haloforms with Hydroxide Ion in 66 2/3% Aqueous Dioxane.[a]

Halide	k X 10^2 (min.$^{-1}$ g.mol.$^{-1}$ liter)[b]			
	25.3°	35.7°	49.9°	0°
$CHCl_3$	0.373	2.25	12.48	
$CHCl_2Br$	9.59	51.9		
$CHClBr_2$	4.84	23.9		
$CHBr_3$	1.92	9.17	52	
$CHFClBr$		~7,500[d]		75.6
CH_2ClBr		~0.015		
CH_2Br_2		~0.004		
CBr_4		<0.6		
$CHCl_2$		<0.001[c]		
CCl_4		<0.0003[c]		

[a] Except where otherwise noted, $[RX]_o \sim 0.022$ M and $[OH^-]_o \simeq 0.025$ M.

[b] Moles of organic halide.

[c] From the data of Hine, J. Am. Chem. Soc., 72, 2438 (1950).

[d] Estimated in text.

tetrahalomethanes. If the S_N2 mechanism were the one followed in the basic hydrolysis, the rate would decrease as the number of halide atoms increased[3]. This was found to be the case in the reaction of haloforms when the nucleophilic reagents are sufficiently weakly basic, for example, piperidine[4] or iodide ion[5].

According to mechanism II (the S_N2 mechanism), there should be no relationship between the basicity of the nucleophilic reagents and the relative rates of reaction of the halides of methane toward these reagents. There should be a relationship, though, according to either mechanism I or III, since the reagent is removing an acidic hydrogen.

The thiocresolate ion was chosen to capture the intermediate carbon dihalide in experiments similar to those in reference 1, in which the thiophenolate ion was used for this purpose. The great increase of the amount of thiocresolate used up when free hydroxide ion is present is shown in table II. This data rules out mechanism II completely, as according to this mechanism the only effect the addition of

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[3]E. D. Hughes, Trans. Faraday Soc., 37, 603 (1941).

[4]P. Petrenko-Kritschenko and V. Opotsky, Ber., 59B, 2131 (1926).

[5]C. H. Thomas, unpublished work from School of Chemistry, Georgia Institute of Technology.

Table II: Effect of Hydroxide Ion Concentration on the Reaction of Sodium p-Thiocresolate with Haloforms.

Haloform	% $p\text{-}CH_3C_6H_4SNa$ reacted		
	$[OH^-]_o \simeq 0$	$[OH^-]_o \sim 0.03$	$[OH^-]_o \sim 0.1$
$CHCl_3$	0.23	20.8	23.0
$CHCl_2Br$	2.5	11.1	23.0
$CHClBr_2$	5.5	16.0	24.2
$CHBr_3$	3.14	11.9	16.7

Table III: Activation Energies of the Basic Hydrolysis of Haloforms.

Haloform	ΔE in Kcal/mole	
	25.3-35.7°	35.7-49.9°
$CHCl_3$	29.8	25.4
$CHCl_2Br$	29.7	
$CHClBr_2$	28.1	
$CHBr_3$	28.5	24.3

hydroxide ion would have on the reaction of sodium p-thiocresolate and a haloform would be competition between the two nucleophilic reagents for the haloforms. This would have to decrease the amount of thiocresolate used up. If the reaction proceeds by mechanism I or III, however, and the thiocresolate is sufficiently reactive toward the carbon dihalide, the addition of free hydroxide would increase the production of the carbon dihalide and therefore greatly increase the rate of disappearance of thiocresolate. Since the latter case is shown by the data of table II, the S_N2 mechanism is ruled out.

It was necessary to prove that the increase in the rate of reaction of p-thiocresol was due to the reaction with the haloform to form p-tolyl orthothiocresolate rather than some other reaction such as a base-catalyzed oxidation to form di-p-tolyl disulfide. This was done by isolating the p-tolyl orthothiocresolate formed in the reaction of p-thiocresol with bromoform in 78% yield (page 18). Bromoform was chosen as it was felt that it was the haloform most likely to give the lowest yield of the desired product.

While mechanism III cannot be ruled out as rigorously as mechanism II, it can be shown to be considerably less likely than mechanism I, by the use of the arguments put forth by Hine[6].

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[6]Jack Hine, J. Am. Chem. Soc., 72, 2438 (1950).

These are:

1. As Hughes[7] has stated, "...first order reaction ... due to bimolecular substitution with water molecules as reagent cannot be upheld...when the much more powerfully basic hydroxide ions are quite inactive." This shows that mechanism III is improbable but does not rule it out entirely since as Hine[8] pointed out, it is possible that water present in large excess may be attacking by an S_N2 mechanism while the hydroxide ion in lesser concentration is not.

2. The mechanism also requires that the trihalomethyl anion present in low concentrations be much more reactive toward water and p-thiocresolate ions by S_N2 attack, while the much greater concentration of haloform is unreactive. It would seem that the neutral haloform molecule would be more susceptible to attack by the negative end of the O-H dipole of water or the negative end of the thiocresolate ion than the negative trihalomethyl carbon atom.

Neither of these factors completely eliminates mechanism III, but do constitute strong support of mechanism I.

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[7]Hughes, op. cit.

[8]Hine, op. cit.

Relative Reactivities of the Haloforms.

The relative reactivities of the haloforms toward basic hydrolysis can be reasonably explained on the basis of the carbon dihalide mechanism. The relative reactivities should be influenced by three factors according to this mechanism:

1. The acidity of the hydrogen.

2. The nature of the halide ion departing in the rate controlling step.

3. The ability of the remaining halogens to speed the rate controlling step by resonance stabilization of the carbon dihalide intermediate.

$$|\bar{X}=\overset{\oplus}{\bar{C}}-\overset{\ominus}{\bar{X}}| \longleftrightarrow |\underline{\bar{X}}-\bar{C}-\underline{\bar{X}}| \longleftrightarrow |\underline{\bar{X}}-\overset{\ominus}{\bar{C}}=\overset{\oplus}{\bar{X}}|$$

The order of decreasing electronegativity of the halogens used, from fluorine to chlorine to bromine should reasonably be the order of decreasing effect on the acidity of their compounds. Therefore CHFClBr should be more acidic than $CHCl_3$, since the difference in electronegativities of fluorine and chlorine is five times as great as the difference between chlorine and bromine, according to the values given by Pauling.[9] Chloroform should be more acidic than $CHCl_2Br$ and $CHCl_2Br$ more acidic than $CHClBr_2$. The fact that $CHCl_2Br$

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[9]L. C. Pauling, The Nature of the Chemical Bond (Ithaca: Cornell University Press, 1940).

should be more acidic than $CHClBr_2$ might seem to conflict with the base-catalyzed deuterium exchange experiments for these two haloforms by Sherman and Bernstein[10] in which the better yield is obtained from $CHClBr_2$. The reaction measured, though, was not only the acidity of the hydrogen, as the study was conducted in a two phase system. As these workers suggest, studies in a single phase system are desirable before any conclusions can be reached concerning this effect.

It is recognized that alkyl bromides are more reactive than the corresponding alkyl chlorides in nucleophilic displacement reactions, therefore it is thought that the CX_3^- would tend to lose a bromide ion more readily than a chloride ion, and a chloride more readily than a fluoride. The increase in reactivity between the chloride and the bromide is usually between 20 and 600 fold.

Consideration of the third factor reveals that there is evidence to show that chlorine is more effective at stabilizing adjacent carbonium ions than either bromine or fluorine[11] and it might be expected to stabilize the carbon dihalide better also. From the above factors, it would be expected that $CHBr_2Cl$ would be more reactive than $CHBr_3$ since

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[10]Sherman and Bernstein, op. cit.

[11]Donald E. Lee; A Thesis, Georgia Institute of Technology, June 1951.

the replacement of a bromine by a chlorine increases the acidity of the hydrogen and stabilizes the carbon dihalide better. The loss of the bromine decreases the rate by reducing the number of bromines available for reaction by one-third. A further increase in rate would be expected in going from $CHClBr_2$ to $CHCl_2Br$, as the additional chlorine further increases the acidity of the hydrogen and the stabilization of the intermediate carbon dihalide. The deactivation caused by the reduction in the number of bromines available for reaction is not too great as there is still one bromine that can leave in the rate controlling step. The reactivity should decrease in going to $CHCl_3$ from $CHCl_2Br$ as there are no bromines available to depart in the rate controlling step. This deactivating factor should overbalance the activation caused by the replacement of the bromines by chlorine. In going from either $CHClBr_2$ or $CHCl_2Br$ to CHFClBr an increase in reactivity might be expected since the fluorine replacing either the bromine or the chlorine would considerably activate the compound by causing the hydrogen to be more acidic. In addition, there is still one bromine available for loss from the CX_3^-. This relative order of reactivities can be seen to be consistent with the rates of reaction in table I. The rates of all of the haloforms at 35.7°C. can be compared to show this. The value for CHFClBr at 35.7°C. can be estimated by using for the activation energy, the average value obtained for the other

haloforms. The rate constant thus obtained is approximately 7,500 $min.^{-1}$ g. mol^{-1} liter.

Activation Energies.

The activation energies of the basic hydrolysis of the haloforms were determined (page 24) and are listed in table III. The large difference in the values for bromoforms and chloroform over two different temperature ranges cannot be explained.

EXPERIMENTAL

Reagents.

Dioxane- Technical dioxane was purified by the method described by Fieser.[12] The boiling point upon distillation under nitrogen was observed to be 101° C. as compared with 101.3° C. as found in Lange's Handbook.[13] The dioxane was stored in brown glass, 2 liter bottles under nitrogen. A 500 millliliter brown glass bottle was filled under nitrogen from the larger containers to provide a source that was exposed to the atmosphere as little as possible.

Chloroform- Eastman Kodak, white label, chloroform was purified by the method described by Fieser.[14] Upon distillation the boiling point was observed to be 60° C. at 739 millimeters. The literature gave the boiling point as 61.2° C.[15].

Chlorodibromomethane- Dow Chemical Company chlorodibromomethane was purified by fractionation under nitrogen in a Todd still have a 25 millimeter diameter, 36 inches high, and packed with 3/32 inch glass helices. The value for the

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[12] L. F. Fieser, Experiments in Organic Chemistry (New York: D. C. Heath and Co., 1941) part II, chapter III.

[13] Lange, N. A., Handbook of Chemistry (Sandusky, Ohio: Handbook Publishers, 1946) p. 448.

[14] Fieser, op. cit.

[15] Lange, op. cit., p. 408.

boiling point is given in the literature[16] as 118-120° C. and that portion that came over at a constant temperature was collected and stored in a brown glass bottle under nitrogen. The boiling point was observed to be 118.5° C. at 738 millimeter pressure.

Bromodichloromethane- Eastman Kodak bromodichloromethane was purified by fractionation in the same manner as dibromochloromethane. It was stored in a brown glass bottle under nitrogen. The boiling point was observed as 89.5° C. at 734 millimeters pressure.

Methylene bromide- Eastman Kodak methylene bromide was purified by fractionation as above. The boiling point was 97° C. at 744.4 millimeters pressure. The compound would have been sufficiently pure without purification as a negligible amount was lost as impurities.

Carbon tetrabromide- Eastman Kodak, C. P., was used as obtained since the melting point was determined to be 90.4° C. as compared with 90.1° C. in the literature.[17]

Bromochloromethane- Eastman Kodak, C. P., was used as obtained.

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[16] Oscar Jacobsen and R. Neumeister, Ber., 15, 601 (1882).

[17] Lange, loc. cit., p. 408.

Bromoform- Baker, C.P., bromoform was fractionated under nitrogen in the same manner as dibromochloromethane. The boiling point was observed to be 149.0° C. at 737.3 millimeters pressure. The value in Lange's Handbook[18] is 150.5° C. at 760 millimeters pressure.

It was found that the bromoform as purified above was not very pure but was quite acidic. It was carefully refractionated under nitrogen and that fraction boiling at 149° C. was collected. It was observed that there was an appreciable percentage of impurities in the apparently pure bromoform sample that was refractionated. A possible explanation of its continued presence is that some high boiling oxidation product of bromoform could decompose to yield an acidic compound that would come over along with the bromoform. A further purification was attempted by fractional crystallization. The unfrozen portion was discarded and the remainder stored under nitrogen. This seemed to produce a pure sample of bromoform, as samples were titrated with standard base and showed no acidity.

The standard solutions of silver nitrate, potassium thiocyanate, carbonate free sodium hydroxide, hydrochloric acid, and iodine in sodium iodide were prepared and standardized by the customary methods.

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[18] Lange, op. cit., p. 387.

Constant Temperature Baths.

The 35.7° and 49.9° C. baths were the standard constant temperature baths employing a large Pyrex jar with an immersion type heater, a stirrer, and a mercury thermo-regulator connected to a relay that controlled the heater. The baths were kept at a constant level by having a steady flow of water coming into the system through a commercial leveling device.

The 25° C. bath was designed to be cooled by tap water and heated by an immersion type heater. A constant flow of tap water and a constant leveling device were constructed. The constant flow was provided by a tube from a 3-necked flask which had a constant head of water from the tap. This was accomplished by having a steady flow of tap water coming in a tube through the top neck and an overflow tube out the middle neck. The constant head was maintained by having the amount of incoming water exceed that amount going to the bath.

The constant leveling device was constructed by blowing a bubble in the center of a 10 centimeter length of glass tubing and placing several small holes in a line perpendicular to the axis of the tubing. The bubble was then enclosed in a layer of copper screen to prevent trash from entering and clogging the aspirator. The device was connected from the top by a piece of rubber tubing to an aspirator.

Whenever the water level rose enough to cover the holes, the vacuum pulled water up the tube and out through the aspirator until the holes were uncovered and air was drawn in.

The temperature was maintained by a control mechanism similar to that used on the other two baths, using a mercury thermoregulator and a relay control.

The baths were calibrated using a -10° C. to 100° C. thermometer standardized by the U. S. National Bureau of Standards. The graduations were approximately 0.7 millimeters apart and each represented 0.5° C. The temperature of the baths were 25.3° C,, 35.7° C., and 49.9° C. All of the readings were 0.05° C. Frequent checking of the temperature of the baths revealed that they were constant within the range of accuracy of the thermometers used, which was in each case 0.02° C.

Preparation of p-Tolyl Orthothioformate.

6.81 grams of p-thiocresol (54.8 millimoles) and 3 milliliters of bromoform were dissolved in 110 milliliters of purified dioxane and 55 milliliters of 1.026 N aqueous sodium hydroxide was added. This solution was refluxed under nitrogen while 10 grams of potassium hydroxide (180 millimoles) in 25 milliliters of distilled water was added. The refluxing was continued for two more hours. The condenser was then reversed and the excess solvent was distilled at about 85° C.

When the temperature rose to 92° C. and a yellow oil started condensing in the upper part of the flask, the distillation was discontinued and the residue cooled. The distillate was titrated with iodine solution to determine the unreacted p-thiocresol. 140 milliliters of distillate required 0.3 milliliters of 0.0608 N iodine solution, and therefore contained 0.02 millimoles of p-thiocresol. The residue was placed in a separatory funnel and the p-tolyl orthothioformate extracted with ether. The ether layer was extracted with concentrated aqueous potassium hydroxide and the aqueous layer with ether. The combined aqueous layer was then titrated with iodine solution. It required 250 milliliters of 0.0608 N iodine and 10.30 milliliters of 0.3001 N iodine to reach the end point. This indicated that 18.29 millimoles of p-thiocresol had not reacted. Therefore 36.5 millimoles had reacted.

The ether layer was concentrated by heating at 50° C. until the ether had evaporated and then at 45° C. and 22 millimeters pressure to remove the other volatile materials. This left an orange-brown solid weighing 8.14 grams, which was recrystallized three times from aqueous ethanol. The light yellow crystals obtained melted at 108-109° C. and weighed 3.60 grams (78%). The melting point of pure p-tolyl

orthothioformate is given as 109° C.[19] and 111° C.[20]

Preparation of Fluorochlorobromomethane.

Approximately 50 grams (210 millimoles) of mercuric fluoride and 40 milliliters (469 millimoles) of chlorodibromomethane were placed in a three-necked flask equipped with a mercury seal stirrer and a reflux condenser. The mixture was first stirred well and then heated slowly with a mantle. Water was passed through the condenser only often enough to keep the temperature of the condenser about 80° C. This was to allow the product, which boiled at approximately 38° C. to pass through, while the chlorodibromomethane, which boiled at 120° C., refluxed. A distilling head, with a thermometer to check the temperature of the gases, was placed on top of the condenser and a decending condenser attached to it. This condenser was cooled with ice water to condense the product. The receiver was placed in ice water and a second receiver was placed after the first in dry ice-acetone. The second receiver was connected to a safety bottle which was connected to a gas absorption tube.

The refluxing was continued for about five hours and the product was collected in the first receiver. A total of about 6 milliliters was collected, which upon purification

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[19]Houben and Schultze, Ber., 44, 3240 (1911).

[20]Arndt, Ann., 384, 338 (1911).

by distillation yielded 5 milliliters, with a boiling point of 36.5-37° C. at 740.1 millimeters.

The refractive index of the fluorochlorobromomethane was 1.4108 at 30° C.

Kinetics.

The basic hydrolysis of the haloforms was assumed to follow the same kinetic order as chloroform, which was found by Hine[21] to be second order, first order with respect to chloroform and first order with respect to hydroxide in 66 2/3% dioxane. Under the conditions of the reactions the products were carbon monoxide and sodium formate. When the reactions were run under the best conditions, the basic hydrolysis of the haloforms studied all obeyed the second order rate equation:

$$V = k_2 (a-x) [b- (3+f) X]$$

where $a = (CHX_3)_o$, $b = (OH^-)_o$, $X = (CHX_3^-)_t$, t = time, f fraction of haloform going to formate, k_2 rate constant in liters/mole of haloform x minutes. The fraction f was determined toward the end of the reaction by comparing the amount of chloride ion formed with the amount of hydroxide ion used up. This was possible since in the reaction to produce carbon monoxide

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[21]Hine, op. cit.

three chloride ions are produced for every three hydroxide ions used up, whereas in the reaction to form sodium formate there are three chloride ions formed for every four hydroxide ions used up.

The equation can be integrated by partial fractions, if f is assumed to be constant (as was found to be applicable by Hine[22] in the case of $CHCl_3$). The resulting equations for the rate constant is:

$$k_2 = \frac{2.303}{t[a(3+f)-b]} \log \frac{b(a-x)}{a[b-(3+f)x]}$$

The rate constant for each point in the kinetic runs was calculated by the above equation and the average of these values was used as the rate constant for that run. The accuracy of the value was stated in terms of the average deviation. The reactions were followed by titrating for hydroxide ion and setting $\Delta(OH^-) = (3+f)x$.

The chloride ion concentration was determined by the method of Volhard whereby a sample is pipetted into a flask containing an excess of aqueous nitric acid. An excess of standardized silver nitrate was added and a few drops of nitrobenzene added to coagulate and coat the precipitated silver chloride. Then a couple of drops of ferric ammonium sulfate

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[22]Hine, loc. cit.

were added as an indicator. Standardized potassium thiocyanate was then added until a red color was observed due to the ferric thiocyanate complex formed after the excess silver ions had been precipitated as the insoluble silver thiocyanate. It was thought that an error could be introduced by reaction of the silver nitrate with the excess haloform, particularly if the haloform contained bromine, as all of the runs had an excess of haloform. It was found that the results were not affected, though. This was done by shaking a small sample of a haloform containing bromine with silver nitrate to produce no precipitate. Furthermore, a known amount of sodium hydroxide was added, more than sufficient to hydrolize all of the haloform, which yielded no precipitate after a reasonable length of time. The excess hydroxide ion was then titrated with standard hydrochloric acid and the total chloride ion concentration determined as before. From these two values the value of $\underline{f}$ could be determined. A comparison of the results with the results of an uncorrected determination of the chloride ion concentration revealed no difference within the range of experimental error. In the determination of the halide ion concentration in the hydrolysis of fluorochlorobromomethane, it was thought that the fluoride ion might interfere by forming a complex with the ferric ions of the indicator. A blank was run using a dilute potassium fluoride solution. The same procedure as above was followed and it was found that equivalent amounts

of silver nitrate and potassium thiocyanate were required. Thus, there was no interference shown by the fluoride ions.

Activation Energies.

The activation energies were calculated by use of the Arrhenius equation:

$$\ln \frac{k_2}{k_1} = \frac{\Delta E}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

where k_1 and k_2 are the rate constants at temperatures T_1 and T_2 in degrees Centigrade, R is the universal gas constant, and ΔE is the activation energy.

The values of the rate constants at 25.3° C. and 35.7° C. for all of the haloforms except CHFClBr were substituted in the above equation. In addition, the values for chloroform and bromoform at 35.7° C. and 49.9° C. were substituted. The values of the activation energies so calculated are listed in table III.

Kinetic Runs.

The reactions were followed by determining the hydroxide ion concentration at various times throughout the runs. This was done by removing a sample of the run and titrating it with hydrochloric acid to the phenolphthalein end point. The initial concentrations, the average rate constants, and the average deviations are tabulated in Table I. Run I is a sample.

Run 1.- Seventy milliliters of purified dioxane, twenty-five milliliters of distilled water and 10 milliliters of approximately 1 N carbonate free sodium hydroxide were shaken together in a flask to make the mixture homogeneous. Enough of this solution was added to a one hundred milliliter volumetric flask to fill it to a point just below the mark. The volumetric flask was then immersed in a constant temperature bath at 35.7° C. for about thirty minutes to allow the contents to reach thermal equilibrium at that temperature. One milliliter of chloroform was pipetted into the volumetric flask which was then withdrawn from the bath and shaken vigorously to accomplish complete mixing. A 5 milliliter sample was extracted with a pipette and placed immediately in a flask containing about 20 milliliters of distilled water at approximately 0° C. This served to freeze the reaction by dilution and by reducing the temperature to a point where the reaction was very much slower. The hydroxide ion concentration was then determined by titrating as stated above. The initial chloroform concentration was determined from the density and volume of the chloroform added. The rate constants were calculated by use of the rate equation. At the time of point 1-9 the reaction was considered complete within experimental error and the chloride ion concentration was determined by the Volhard method (page 22). To a 5 milliliter sample of the run, 20 milliliters of 0.0461 N silver nitrate were added and 27 milliliters of 0.0273 N

KSCN were required to reach the end point. Therefore the chloride ion concentration was 0.0310 moles/liter.

The comparison of the chloride ion produced with the amount of hydroxide ion used up showed that the reaction had gone 90.6% by the route of three hydroxide ions per chloroform and 9.4% by the route of four hydroxide ions per chloroform. This value was consistant with that obtained by Hine.[23]

After several of the other haloforms were run following the procedure above, it was found that some of them reacted far too rapidly so a change was made in the procedure, to reduce the concentrations of the reactants. The procedure used in Run 12 for chloroform was used as the standard procedure for the rest of the haloforms, in so far as possible, as it was desired to compare the rates of hydrolysis of the various haloforms under the same conditions. This procedure also eliminated the error introduced in reactions that were quite rapid, where the initial determination of the hydroxide ion concentrations was not exact. This error was caused by the reaction of some of the hydroxide ion in the time interval between adding the haloform and titrating the hydroxide ion.

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[23]Hine, loc. cit.

Run 12- In this run 65 milliliters of purified dioxane (page 14), 32 milliliters of distilled water, and 3 milliliters of approximately 1 N carbonate free sodium hydroxide were added to a 100 milliliter volumetric flask which was placed in the constant temperature bath at 35.7 ± 0.02° C. and allowed to approach thermal equilibrium. Then the flask was removed from the bath and filled to just below the mark with 65% aqueous dioxane and again allowed to reach thermal equilibrium. The quantity of solution was adjusted to just equal 100 milliliters at 35.7° C. A 5 milliliter sample was then extracted and titrated to the phenolphthalein end point with 0.0276 N HCL. This required 5.30 milliliters of acid, therefore the initial hydroxide ion concentration was 0.0278 moles/liter. One milliliter of purified $CHCl_3$ (page 14) was pipetted into a weighed 25 milliliter volumetric flask and the flask weighed again to determine the weight of the $CHCl_3$ added. Enough dioxane was then added to fill the flask almost to the mark and the flask was placed in the constant temperature bath at 35.7° C. and allowed to approach thermal equilibrium. It was then made exactly up to the mark with dioxane at 35.7° C. and again allowed to reach thermal equilibrium. Five milliliters of this solution was then pipetted into the reaction flask above, which was then shaken to produce homogeneity. Twelve milliliters samples were extracted periodically and titrated to the phenolphthalein end point with 0.0276 N HCL to determine the

hydroxide ion concentration and thus follow the reaction. These samples were pipetted into about 20 milliliters of water at approximately 0° C. to stop the reaction as explained under Run 1. In Run 12 the initial $CHCl_3$ concentration was 0.0236 moles/liter.

The basic hydrolysis of each of the haloforms was followed until the calculated constants were reproducible. It was considered satisfactory if the values from two runs agreed closely and the constants for the various points of each run had less than 5% average deviation. The data for the runs are tabulated in the Appendix in tables IV-XLIX and LXIII-LXIV.

Reaction of Sodium p-Thiocresolate with the Haloforms.

The effect of hydroxide ion on the rate of reaction of sodium p-thiocresolate with the haloforms was studied. Each of the haloforms was allowed to react with p-thiocresol in aqueous dioxane in the presence of sufficient sodium hydroxide to convert most of the p-thiocresolate to sodium salt, for a time corresponding to that time required for the basic hydrolysis to go essentially to completion. The haloform was then allowed to react under the same conditions with an excess of hydroxide ion present for the same length of time. The reaction was followed by determining the sodium p-thiocresolate concentration at the beginning and at the end of the reaction. This was accomplished by titrating a sample in methanol,

containing a little acetic acid, with 0.0608 N I_2 in sodium iodide solution. The runs were made under nitrogen to reduce oxidation. The reactions were compared on the basis of the percent of p-thiocresolate used up in each case. These values can be found in Table III and the data in Tables L-LXII.

Run 47 is typical of the runs having an excess of hydroxide ion present. Nineteen milliliters of 1.026 N NaOH, 16 milliliters of distilled water, 70 ml of purified dioxane and about 2 grams of p-thiocresol were placed in a flask and shaken well to give a homogeneous solution. Enough of this was placed in a 100 milliliter volumetric flask to bring the volume to exactly 100 milliliters after allowing the flask to equilibrate at 35.7° C. for thirty minutes. A 5 milliliter sample was then extracted (10 ml samples were used in all subsequent runs) and placed in about 20 milliliters of methanol containing 1 milliliter of acetic acid and titrated immediately with 0.0608 N iodine in sodium iodide solution until the yellow color of the iodine persisted. Methanol was added as necessary to keep the solution homogeneous. At time zero, 1 milliliter of chloroform was pipetted into the reaction flask, which was then shaken well. Another determination of the p-thiocresol was made when the reaction had proceeded long enough for the basic hydrolysis to be complete, as compared with the earlier runs. The difference in the initial and the final concentrations, divided by the initial concentration gave the percent of the p-thiocresol used up.

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APPENDIX I

Calculations

SAMPLE CALCULATION OF RATE CONSTANT

The calculation is made for Run 40, point 40-2. The initial hydroxide ion concentration was 0.0293 moles/liter and the reaction went completely by the route of 3 hydroxide ions per mole of haloforms. At point 40-2 the hydroxide ion concentration was 0.0283 moles/liter. Therefore $\Delta OH = 0.0010$ moles/liter. The value of x can be calculated from $x = OH/3+f$, which in this case gives $x = 0.00032$. The value of f is zero.

Substituting these values in the rate equation (page 22):

$$k_2 = \frac{2.303}{t\,[(3+f)\,a-b]} \log \frac{b\,(a-x)}{a\,[b-(3+f)x]}$$

gives:

$$k_2 = \frac{2.303}{10\,[3(0.0277)-0.0292]} \log \frac{.0293(\,.0227-.0003)}{.0227\,[.0293-3(\,.0003)]}$$

which simplifies to:

$$k_2 = 4.82 \times 10^{-2} \text{ min.}^{-1} \text{ g. mol.}^{-1} \text{ liter.}$$

APPENDIX II

Tables

Table IV: Run 1- Kinetic Run of the Basic Hydrolysis of Chloroform in 66 2/3% Aqueous Dioxane.

Initial chloroform concentration.....0.0954 M
Initial hydroxide ion concentration..0.123 N

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	k ($min.^{-1}$ $g.mol.^{-1}$ l.)
1-1	11-0949	17.30	0	
1-2	1109	11.50	80	0.0144
1-3	1226	7.78	157	0.0148
1-4	1326	5.90	217	0.0150
1-5	1428	4.75	279	0.0143
1-6	1529	3.45	340	0.0148
1-7	1629	2.72	400	0.0146
1-8	12-0859	0.12	1390	0.0125[a]
1-9	14-0849	0.02	4260	
		Average		0.0147±1.3%

[a] Not averaged

Procedure: The procedure followed is discussed under Kinetic Runs.

Table V: Run 2- Kinetic Run of the Basic Hydrolysis of $CHClBr_2$ in 66 2/3% Aqueous Dioxane.

Initial $CHClBr_2$ concentration.....0.116 M

Point	Time Sample Extracted	Milliliters .0276 N HCl	Time (minutes)	k ($min.^{-1}$ $g.mol.^{-1}$ l.)
2-0	0911	16.63	0	
2-1	0941	5.17	30	0.126
2-2	1132	.12	141	

Procedure: This run was made following the same procedure as Run 1 except that $CHClBr_2$ was used instead of $CHCl_3$. The run was used only as a rough approximation of the rate, as the reaction proceeded so rapidly and CO evolved so rapidly that the initial shaking created enough pressure to blow the top out of the flask along with some of the solution. The density of chlorodibromomethane was not readily available and was determined by weighing a 5 milliliter sample. It was found to weigh 12.10 grams at room temperature, therefore the density was 2.42 gram/cc. An approximate rate constant was calculated from the first point.

Table VI: Run 3- Kinetic Run of the Basic Hydrolysis of $CHClBr_2$ in 66 2/3% Aqueous Dioxane.

Initial $CHClBr_2$ concentration.....0.116 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	k ($min.^{-1}$ $g.mol.^{-1}$ $l.^{-1}$)
3-0	1205	15.23	0	
3-1	1236	3.10	31	0.160

Procedure: This run was made in the same way as run 2, but again proceeded too rapidly to follow well. Since the reaction was about 80% complete in 31 minutes, it was decided to reduce both the hydroxide ion and the chlorodibromomethane concentrations.

Table VII: Run 4- Kinetic Run of the Basic Hydrolysis of $CHClBr_2$ in 66 2/3% Aqueous Dioxane.

Initial $CHClBr_2$ concentration..... 0.0233 M
Initial hydroxide ion concentration.... 0.0291 N

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	k ($min.^{-1}g.mol.^{-1}l.$)
4-0	0932	12.65	0	
4-1	0942	10.66	10	0.256
4-2	1012	6.58	40	0.268
4-3	1042	4.38	70	0.256
4-4	1116	2.90	104	0.255
4-5	0106	.92	214	0.212[a]

[a] Not Averaged Average 0.250

Procedure: The procedure followed in this run was designed to reduce the concentrations from the procedure of Run 1. It was found experimentally that the following amounts of chemicals, when mixed, yield exactly 100 milliliters of solution at 35.7° C.: 63 milliliters of purified dioxane, 31 milliliters of distilled water and 3 milliliters of approximately 1 N NaOH. These were mixed, added to a 100 milliliter volumetric flask, and 1 milliliter extracted. Then the flask and contents were allowed to reach thermal equilibrium at 35.7° C. When 5 ml. of a solution of 1 ml. of $CHClBr_2$ diluted to 25 ml. at room temperature with dioxane was added, the volume was 100 ml. After shaking a 12 ml. was titrated with 0.0276 N HCl to determine $(OH^-)_o$.

Table VIII: Run 5- Kinetic Run of the Basic Hydrolysis of CHFClBr in 66 2/3% Aqueous Dioxane.

Procedure: This run was conducted following the procedure of Run 1 and was only to obtain an approximation of the rate. The compound was therefore not purified. The reaction took place so rapidly that the top of the volumetric flask was blown off when the flask was shaken. The addition of the initial 5 milliliters sample to the cold distilled water containing phenolphthalein did not produce the characteristic pink color of a basic solution. This indicated that all of the hydroxide ion was used. To check this observation, another run was made.

Table IX: Run 6- Kinetic Run of the Basic Hydrolysis of CHFClBr in 66 2/3% Aqueous Dioxane

Procedure: The same procedure as for Run 5 was followed for Run 6. The same results were obtained as before. The reaction was vigorous and the 5 milliliters sample was extracted as rapidly as possible and placed in the cold water containing phenolphthalein. No color change was observed. This indicated that the reaction was far too rapid to be followed. It was thought that the extreme reactivity might be due to a reactive decomposition product or impurity. To determine if this could be the cause, enough sodium hydroxide was added to a 50 milliliter sample to the run to provide slightly greater than four hydroxide ions for each mole of fluorochlorobromomethane. This required 23 milliliters of approximately 1 N sodium hydroxide. The halide ion concentration was determined by the Volhard method. Two milliliter sample was extracted and 20 milliliters of 0.0461 N $AgNO_3$ were added. 19.7 milliliters of 0.0273 N KSCN required to reach the desired end point. Therefore, the total halide ion concentration was 0.288 moles/liter. An impurity must have been present, since the total possible halide ion concentration was 0.275 moles/liter.

Table X: Run 7- Kinetic Run of the Basic Hydrolysis of $CHCl_2Br$ in 66 2/3% Aqueous Dioxane.

Initial $CHCl_2Br$ concentration.....0.02 M
Initial hydroxide ion concentration.0.0256 N

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	k ($min.^{-1}$ $g.mol.^{-1}$ l.)
7-0	1353	11.14	0	
7-1	1403	7.99	10	0.505
7-2	1423	4.60	30	0.482
7-3	1508	1.80	75	0.428
7-4	1613	.53	140	0.419

Procedure: The procedure followed was the same as for Run 4. It was believed that the decrease in the rate constant k was due to the technique used in determining the initial hydroxide ion concentration since some of the hydroxide ion could be used up by a rapid reaction before determining the concentration. This was shown by the determination of the halide concentration as 0.0305 N. This was greater than the original hydroxide ion concentration which was 0.0256 N.

Table XI: Run 9- Kinetic Run of the Basic Hydrolysis of CH_2ClBr in 66 2/3% Aqueous Dioxane.

Initial CH_2ClBr concentration.....0.1540 M
Initial hydroxide ion concentration.0.0956 N

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	k x 10^4 (min^{-1} $g.mol^{-1}$ l.)
9-0	27-1548	17.32	0	
9-1	28-0902	16.00	1034	2.10[a]
9-2	29-1041	14.80	2574	1.69[a]
9-3	30-0831	14.21	3834	1.44
9-4	2-0941	12.63	6784	1.26
9-5	3-1331	11.75	8454	1.25
9-6	6-1108	9.80	12631	1.37
9-7	16-1245	5.20	27128	1.35
9-8	31-1925	2.10	49128	1.37
		Average		1.48±14%

[a] Not averaged

Procedure: The procedure followed for this run was the same as that used for chloroform in Run 1. A Volhard determination was made toward the end of the run. A 10 milliliter sample of the run required 19 milliliters of 0.0461 N $AgNO_3$ and 6.60 milliliters of 0.0273 N KSCN. This corresponded to a halide ion concentration of 0.0696 N. Therefore, the reaction went by the route of 2.41 moles of hydroxide ions per mole of CH_2ClBr.

The values of the rate constants were sufficiently close when calculated according to the second order rate equation, as only an order of magnitude was actually required.

Table XII: Run 10- Kinetic Run of the Basic Hydrolysis of CBr_4 in 66 2/3% Aqueous Dioxane.

Initial CBr_4 concentration.....0.0994 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	k ($min^{-1}g.mol^{-1}l.$)
10-0	2-1506	14.45	0	
10-1	1616	10.80	70	.0611
10-2	3-1353	.18	1367	

Procedure: This run was made with about the same concentrations as Run 1. Since carbon tetrabromide is a solid, a slightly different technique was used.

Twice the amount of CBr_4 necessary to produce the concentration desired (0.1 N) was weighed in a weighing bottle and 10 ml. of dioxane added. A 5 ml. sample of this was then added to the reaction flask at time zero. A volumetric flask was calibrated at the 95 ml. mark. The flask was then filled at room temperature to just below this mark with a mixture of 65 ml. of dioxane, 10 ml. of approximately 1 N NaOH, and 25 ml. of distilled water. The flask and contents were allowed to reach thermal equilibrium at 35.7° C. and the level was adjusted exactly to 95 ml. The 5 ml. sample of dioxane-CBr_4 at room temperature was then added. The flask was then shaken and a 5 ml. sample extracted and titrated with 0.0276 N HCl. The reaction was not followed closely enough for any rate constant to be calculated.

Table XIII: Run 11- Kinetic Run of the Basic Hydrolysis of CH_2Br_2 in 66 2/3% Aqueous Dioxane.

Initial CH_2Br_2 concentration.....0.1435 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	k ($min.^{-1}g.mol.^{-1}l.$)
11-0	3-1837	17.10	0	
11-1	1857	17.10	20	
11-2	1927	17.10	50	
11-3	4-0937	16.90	900	3.72×10^{-5}
11-4	6-1102	16.24	3700	3.43
11-5	16-1252	13.50	18210	2.98[a]
11-6	11-1000	7.77	54043	4.01
11-7	13-1020	7.42	56943	4.04
		Average		3.64±9.4%

[a] Not averaged

Procedure: This run was made in the same manner as Run 9. A Volhard determination was made at point 11-7 or after the run had progressed about forty days. A 10 milliliter sample required 10 milliliters of 0.0461 N $AgNO_3$ and 2.62 milliliters of 0.0273 N KSCN. This corresponded to a bromide ion concentration of 0.0389 N. This indicated that the reaction went by the route of 2.75 hydroxide ions per methylene bromide molecule.

The second order rate constants calculated from this data were satisfactory.

Table XIV: Run 12- Kinetic Run of the Basic Hydrolysis of $CHCl_3$ in 66 2/3% Aqueous Dioxane.

Initial CHCl concentration..... 0.0236 N

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (Minutes)	$k \times 10^2$ ($min.^{-1} g.mol.^{-1} l.$)
12-0	6-1148	(5.30)*	0	
12-1	1208	11.83	20	1.332a
12-2	1351	10.14	123	2.060
12-3	1553	8.65	245	1.980
12-4	1840	7.03	412	1.976
12-5	7-0832	2.89	1244	1.933
12-6	9-1310	.40	4402	

a- Not averaged Average 1.987×10^{-2} - 1.8%

Procedure: The procedure for this run was discussed in Kinetic Runs.

*5 ml. Sample

Table XV: Run 13- Kinetic Run of the Basic Hydrolysis of $CHCl_3$ in 66 2/3% Aqueous Dioxane.

Initial $CHCl_3$ concentration..... 0.0236 N

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (Minutes)	$k \times 10^2$ ($min.^{-1} g.mol.^{-1} l.$)
13-0	6-1534	(5.30)	0	
13-1	1557	11.72	23	2.030
13-2	1855	9.10	201	2.162
13-3	7-0824	3.60	1010	2.002
13-4	9-1427	.60	4253	

Average 2.064×10^{-2} - 3.1%

Procedure: This run was made in exactly the same manner as Run 12, and was run as a check for the value of the average rate constant. It was decided to make at least two runs for each haloform under each set of conditions to see if the values were reproducible. In cases where they were not, corrections to the procedure were made until reproducible results were obtained.

At point 13-4 a 10 ml. sample plus 8 ml. of 0.0461 N $AgNO_3$ required 4.12 ml. of 0.0273 N KSCN. Therefore, Cl^- - 0.0266 and f - 0.151.

Table XVI: Run 14- Kinetic Run of the Basic Hydrolysis of $CHClBr_2$ in 66 2/3% Aqueous Dioxane

Weight bottle - dioxane - $CHClBr_2$.....	32.6852 grams
Weight bottle - dioxane.....	30.3112
Weight $CHClBr_2$.....	2.3740

Initial $CHCLBr_2$ concentration..... 0.0228 N

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (Minutes)	$k(min.^{-1}g.mol.^{-1}l.)$
14-0	6-1816	(5.30)	0	0.234
14-1	1826	10.30	10	0.234
14-2	1845	7.75	29	0.228
14-3	1956	3.30	100	0.220
14-4	7-0822	0.20	846	

Average 0.232 - 1.3%

Procedure: This run followed the same procedure as Run 12. To determine the halide ion concentration, a 10 ml. sample required 8 ml. of 0.0461 N $AgNO_3$ and 3.15 ml. of 0.0273 N KSCN. This indicated a halide ion concentration of 0.0284 N. Since it had previously been proven that the $AgNO_3$ did not react with the unhydrolyzed haloform, it was decided that this error could only be due to an acid oxidation product of the haloform. A 10 ml. sample required 0.08 ml. of0.0503 N NaOH. This correction applied to the halide ion concentration made it equal to the hydroxide ion concentration, therefore, making f equal to zero.

Table XVII: Run 15- Kinetic Run of the Basic Hydrolysis of $CHClBr_2$ in 66 2/3% Aqueous Dioxane.

Initial $CHClBr_2$ concentration..... 0.0228 N

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (Minutes)	$k(min.^{-1}g.mol.^{-1}l.)$
15-0	6-1819	(5.28)	0	
15-1	1831	10.15	12	0.219
15-2	1849	7.79	30	0.232
15-3	2001	3.15	102	0.260
15-4	7-0839	0.20	860	

Average 0.237 - 6.3%

Procedure: The same procedure was followed as for Run 14. A Volhard titration used a 10 ml. sample and required 8 ml. of 0.0461 N $AgNO_3$ and 3.15 ml. of 0.0273 N KSCN. The halide ion concentration was, therefore, 0.0282 N. Since this was greater than the hydroxide ion concentration, the oxidation correction was determined. A 10 ml. sample required 0.10 ml. of 0.0503 N NaOH. The corrected halide ion concentration was 0.0277 and thus f was zero

Table XVIII: Run 16- Kinetic Run of the Basic Hydrolysis of CBr_4 in 66 2/3% Aqueous Dioxane.

Weight of flask - CBr_4 ..... 22.1414 grams
Weight of flask 21.3421
Weight of CBr_4 ..... 0.7993

Initial CBr_4 concentration ..... 0.00482 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	$k \times 10^2$ ($min.^{-1} g.mol.^{-1} l.$)
16-0	10-1315	(5.00)	0	
16-1	1329	8.40	14	
16-2	1348	8.02	33	1.220*
16-3	1710	6.10	235	0.685
16-4	2300	4.59	585	0.570
16-5	11-1050	3.38	1295	0.422
16-6	13-1540	2.04	4475	0.221*

*Not averaged Average 0.624

Procedure: The same general approach as Run 10 was followed with several exceptions: (1) The reaction flask was painted black on the outside to exclude light. (2) The run was made under N_2. (3) The CBr_4 was weighed and diluted in a dark room. (4) The basic aqueous dioxane solution was allowed to equilibrate at 35.7°C. and 100 ml. pipetted into the volumetric flask. A 5 ml. sample was titrated with 0.0276 N HCl to determine the initial hydroxide ion concentration. A 5 ml. sample of the CBr_4- dioxane was then added at time zero. In determining the Br^- a 10 ml. sample required 8 ml. of 0.0461 N$AgNO_3$ and 6.80 ml. of 0.0273 N KSCN. Br^- was therefore 0.0183 moles/liter, which indicated that the reaction proceeded

entirely by the route of 5 hydroxide ions per CBr_4. The rate constants were calculated using point 16-1 as the initial point. The average rate constant obtained was only meant to be a maximum value for the hydrolysis.

Table XIX: Run 17- Kinetic Run of the Basic Hydrolysis of $CHClBr_2$ in 66 2/3% Aqueous Dioxane.

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	k($min^{-1}g.mol^{-1}l.$)
17-0	1439	(5.10)	0	
17-1	1447	10.15	8	0.257
17-2	1454	9.07	15	0.252
17-3	1506	7.50	27	0.256
17-4	1524	6.12	45	0.235
17-5	1558	4.16	79	0.230
17-6	1634	2.93	115	0.250
			Average	0.247 - 4.3%

Procedure: This run followed the same procedure as Run 14. The $CHClBr_2$ concentration was exactly the same.

Table XX: Run 18- Kinetic Run of the Basic Hydrolysis of $CHCl_2Br$ in 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHCl_2Br$..... 34.2316 grams
Weight flask dioxane.....?..... 32.2643
Weight $CHCl_2Br$..... 1.9673

Initial $CHCl_2Br$ concentration..... 0.0240 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	k($min.^{-1}$ $g.mol.^{-1}$ $l.$)
18-0	1855	(5.40)	0	
18-1	1900	10.30	5	0.511
18-2	1905	9.00	10	0.461
18-3	1920	5.73	25	0.484
18-4	1935	4.00	40	0.463
18-5	2148	0.82	173	0.326
			Average	0.48

Procedure: This run followed the same procedure as Run 12. A 10 ml. sample required 8 ml. of 0.0461 N $AgNO_3$ and 1.7 ml. of 0.0273 N KSCN. The halide ion concentration was 0.0322 moles/liter, which was greater than the hydroxide ion concentration.

Table XXI: Run 19- Kinetic Run of the Basic Hydrolysis of $CHBr_3$ in 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHBr_3$..... 32.9495 grams
Weight flask dioxane..... 30.1602
Weight $CHBr_3$..... 2.7893

Initial $CHBr_3$ concentration..... 0.0221 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	$k \times 10^2$ ($min.^{-1} g.mol.^{-1} l.$)
19-0	20-1919	(5.35)	0	
19-1	1930	11.55	11	6.88
19-2	1949	10.59	30	6.66
19-3	2019	9.30	60	6.55
19-4	2124	6.09	125	9.82
19-5	21-1029	1.05	910	

Average 6.7

Procedure: The procedure of Run 12 was followed. A 10 ml. sample of the run required 8 ml. of 0.0461 N $AgNO_3$ and 3.65 ml. of 0.0273 N KSCN. The bromide ion concentration was therefore 0.0269 and f .125.

The values of the rate constant were not all consistant.

Table XXII: Run 20- Kinetic Run of the Basic Hydrolysis of $CHBr_3$ in 66 2/3% Aqueous Dioxane

Initial $CHBr_3$ concentration..... 0.02207 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	$k \times 10^2$ ($min.^{-1} g.mol.^{-1} l.$)
20-0	23-1330	(5.25)	0	
20-1	1340	14.00	10	9.292
20-2	1400	10.30	30	6.954
20-3	1415	9.67	45	6.894
20-4	1520	7.50	110	7.701
20-5	1640	5.50	190	6.423
20-6	24-1300	.41	1410	

Procedure: This run also followed the procedure of Run 12 and was run as a check on Run 19. The bromoform concentration was the same as before, as the sample was extracted from the same 25 ml. volumetric flask. A 10 ml. sample required 8 ml. of 0.0461 N $AgNO_3$ and 3.50 ml. of 0.0273 N KSCN. Br^- was 0.0290 moles/liter. Since this was too high to explain in terms of the hydrolysis reaction, it appeared that considerable oxidation had taken place. It was decided to conduct the future runs of bromoform under nitrogen to reduce the oxidation. The values of the tabulated rate constants were calculated using the hydroxide ion to haloform ratio determined in Run 24.

Table XXIII: Run 21- Kinetic Run of the Basic Hydrolysis of $CHCl_2Br$ in 66 2/3% Aqueous Dioxane.

Initial $CHCl_2Br$ concentration.....

Weight flask dioxane $CHCl_2Br$..... 33.7865 grams
Weight flask dioxane..... 31.8904 grams
Weight $CHCl_2Br$..... 1.8961 grams

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	k($min^{-1}g.mol^{-1}l.$)
21-0	24-1517	(5.25)	0	
21-1	1521	10.60	4.0	.432
21-2	1527	8.59	10.0	.508
21-3	1537	6.28	20.0	.521
21-4	1552	4.06	35.0	.532
21-5	1622	2.00	65.0	.512
			Average	.518

Procedure: The procedure followed was the same as Run 12. The rate constants were satisfactory, if the first one was ignored. This was justifiable because of the short time interval and consequent large percentage error possible. To a 10 ml. sample of the run were added 8 ml. of 0.0461 N $AgNO_3$ and 3.61 ml. of 0.0273 N KSCN. Therefore, the halide ion concentration was 0.0270 moles/liter and f was 0.056.

Table XXIV: Run 22- Kinetic Run of the Basic Hydrolysis of $CHCl_2Br$ in 66 2/3% Aqueous Dioxane.

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	$k(min.^{-1}g.mol.^{-1}l.)$
22-0	24-1840	(5.31)*	0	
22-1	1845	10.18	5	.501
22-2	1850	8.40	10	.546
22-3	1900	6.11	20	.538
22-4	1915	4.15	35	.508
22-5	1940	2.20	60	.505
			Average	.520

Procedure: This run was made exactly the same as Run 21. The initial $CHBrCl_2$ concentration was the same as the same dioxane-$CHBrCl_2$ sample was used. The rate constants were consistant and agreed with those of Run 21. A Volhard titration required 8 ml. of 0.0461 N $AgNO_3$ and 3.60 ml. of 0.0273 N KSCN for a 10 ml. sample of the run. The halide ion concentration was 0.0270 moles/liter and f was 0.10.

Table XXV: Run 23- Kinetic Run of the Basic Hydrolysis of $CHBr_3$ in 66 2/3% Aqueous Dioxane

Initial $CHBr_3$ concentration..... 0.02214 moles/liter

Weight flask	dioxane $CHBr_3$.....	35.1800
Weight flask	dioxane.....	32.3821
	Weight $CHBr_3$.....	2.7979

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	k X 10^2 k(Min.$^{-1}$g.mol.$^{-1}$l.)
23-0	3-1857	5.20	0	
23-1	1907	11.30	10	6.232
23-2	1922	10.59	25	6.276
23-3	1947	9.50	50	6.152
23-4	2052	7.30	115	6.165
23-5	2147	4.92	170	
23-6	4-1222	0.10	1045	

Average 6.206×10^{-2} - 0.8%

Procedure: This run followed Runs 19 and 20. The bromide ion concentration used in the rate calculation of the rate constants was determined by Run 24. Rate constants were consistant, if last point was ignored.

Table XXVI: Run 24- Kinetic Run of the Basic Hydrolysis of $CHBr_3$ in 66 2/3% Aqueous Dioxane.

Point	Time Sample Extracted	Milliliters 0.0276 N HCL	Time (minutes)	$k(min.^{-1}g.mol.^{-1}l.)$
24-0	3-1855	5.20	0	
24-1	4-1230	0.65	1050	

Procedure: This run was made to determine the route of the reaction. The procedure followed was the same as that followed for Runs 19 and 20 with the following exception: (1) The run was made under nitrogen, (2) No points were taken early in the run, as only the amount of hydroxide ion used up in the hydrolysis was desired. A 10 ml. sample at point 24-1 required 8 ml. of 0.0461 N $AgNO_3$ and 4.38 ml. of 0.0273 N KSCN. The bromide ion concentration was therefore 0.0239 moles/liter, which corresponds to the reaction going 76.7% by the route of three hydroxide ions for each bromoform and 23.3% by the route of four hydroxide ions per bromoform. This value was used for all of the bromoform runs, as it was felt that it was too difficult to get accurate results from runs exposed to oxidation so frequently.

Table XXVII: Run 25- Kinetic Run of the Basic Hydrolysis of $CHBr_3$ in 66 2/3% Aqueous Dioxane

Weight of flask dioxane $CHBr_3$..... 34.7831
Weight of flask dioxane..... 32.0035
Weight $CHBr_3$..... 2.7796

Initial $CHBr_3$ concentration..... 0.02199 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	$k \times 10^2$ ($min.^{-1} g.mol.^{-1} l.$)
25-0	25-1550	(4.25)	0	
25-1	1600	6.95	10	21.73
25-2	1615	6.43	25	13.45
25-3	1640	5.68	50	10.59
25-4	1730	4.24	100	10.18
25-5	1820	3.38	150	9.480
25-6	2050	1.87	300	8.57

Procedure: This run was made in the same manner as Runs 19, 20, and 23 with the following exceptions: (1) The run was made under nitrogen. While each point was being taken the reaction flask was flushed with nitrogen by allowing the nitrogen to pass slowly into the neck of the flask from a side arm connected just above the 100 ml. mark on the neck of the volumetric flask. This constant flow of nitrogen was to prevent any air from coming in contact with the system while samples were being extracted and left the system in contact with an atmosphere of nitrogen between points. (2) Ten milliliter samples were extracted instead of the usual 12 ml. The rate constants were unsatisfactory, as they decreased as the run proceeded, indicating that the bromoform added might have oxidized.

Table XXVIII: Run 26- Kinetic Run of the Basic Hydrolysis of $CHBr_3$ in 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHBr_3$..... 33.8416
Weight flask dioxane..... 31.5493
Weight $CHBr_3$..... 2.2923

Initial $CHBr_3$ concentration..... 0.01814 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	$k \times 10^2$ ($min.^{-1} g.mol.^{-1} l.$)
26-0	4-1516	(4.17)	0	
26-1	1526	7.03	10	13.69
26-2	1541	6.53	25	10.95
26-3	1606	5.85	50	9.65
26-4	1642	5.05	86	9.04
26-5	1716	4.47	120	8.64

Procedure: The same procedure was followed as Run 25. The bromoform was refractionated before use. The values for the rate constant again decreased as the run progressed. The bromoform-dioxane solution was tested for acidity to see if the bromoform had oxidized in the short time between purification and use. A 5 ml. sample required 2.25 ml. of 0.0506 N NaOH. This corresponds to 0.1138 milliequivalents of hydroxide ions used up immediately. Considering that one bromoform was used up for each three hydroxide ions reduced the initial bromoform concentration to 0.0178 M and the initial hydroxide ion concentration to 0.0268 N. The application of these corrections was insufficient to get a constant value for the rate constant.

Table XXIX: Run 27- Kinetic Run of the Basic Hydrolysis of $CHCl_3$ in 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHCl_3$..... 27.5414
Weight flask dioxane..... 26.0993
Weight $CHCl_3$..... 1.4421

Initial $CHCl_3$ concentration..... 0.02416 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes	$k \times 10^3$ ($min.^{-1} g.mol.^{-1} l.$)
27-1	10-1049	(5.20)	0	
27-2	1119	11.83	30	1.506*
27-3	1209	11.57	80	6.192
27-4	1449	11.17	240	5.038
27-5	1849	10.40	480	5.610
27-6	11-0825	8.09	1296	6.323
27-7	13-1049	4.10	4320	5.787

*Not averaged Average 5.790 - 6.5%

Procedure: This run was conducted in the same manner as Run 12 except that it was run at 25.3°C.

Table XXX: Run 28- Kinetic Run of the Basic Hydrolysis of $CHClBr_2$ in 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHClBr_2$..... 33.9926
Weight flask dioxane..... 31.5209
Weight $CHClBr_2$..... 2.4717

Initial $CHClBr_2$ concentration..... 0.02373 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	($min.^{-1}g.mol.^{-1}l.$)
28-0	10-1416	(5.23)	0	
28-1	1431	11.50	15	3.406*
28-2	1459	10.40	43	4.590
28-3	1602	8.40	106	4.952
28-4	1856	5.22	280	4.748
28-5	2149	3.45	453	4.644
28-6	11-0831	1.24	1095	3.838*

*Not averaged Average 4.733 - 1.9%

Procedure: The same procedure as that established in Run 12, for the standard runs were followed except that the temperature of the thermostat was 25.3°C. The fraction of the haloform going to formate was assumed to be the same as that determined at 35.7°C.

Table XXXI: Run 29- Kinetic Run of the Basic Hydrolysis of $CHCl_2Br$ in 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHCl_2Br$.....33.0002
Weight flask dioxane.....31.0322
Weight $CHCl_2Br$..... 1.9680

Initial $CHCl_2Br$ concentration..... 0.02402 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	$k_1 \times 10^2$ ($min.^{-1}$ $g.mol.^{-1}$ l.)
29-0	10-1945	(5.14)	0	
29-1	1955	11.05	10	7.914[a]
29-2	2033	8.40	48	9.871
29-3	2116	6.10	91	10.719
29-4	2222	3.08	157	13.967
29-5	2328	2.85	223	10.390
29-6	11-0835	0.63	770	
		Average		11.24±12.2%

[a] Not averaged

Procedure: The procedure followed was the same as Run 28.

Table XXXII: Run 30- Kinetic Run of the Basic Hydrolysis of $CHCl_3$ in 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHCl_3$.....37.9607
Weight flask dioxane.....36.5299
Weight $CHCl_3$..... 1.4308

Initial $CHCl_3$ concentration.....0.02397 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	$k_1 \times 10^2$ ($min.^{-1} g.mol.^{-1} l.$)
30-0	10-2205	(5.20)	0	
30-1	2210	11.50	5	8.336[a]
30-2	2215	10.90	10	11.429
30-3	2240	8.63	35	12.876
30-4	2315	6.34	70	13.232
30-5	2344	5.24	99	12.525
30-6	11-0845	0.60	640	
		Average		12.52±4.3%

[a] Not averaged

Procedure: This run was conducted in the same manner as Run 12 except that it was made at 49.9° C. The first point in the run was ignored in calculating the average value of the rate constant.

Table XXXIII: Run 31- Kinetic Run of the Basic Hydrolysis of $CHCl_3$ in 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHCl_3$.....33.6525
Weight flask dioxane.....32.2019
Weight $CHCl_3$..... 1.4506

Initial $CHCl_3$ concentration.....0.02430 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	$k_1 \times 10^3$ ($min.^{-1} g.mol.^{-1} l.$)
31-0	14-1650	(5.21)	0	
31-1	2223	9.05	333	3.586
31-2	15-0925	7.45	995	3.943
31-3	16-1055	5.20	2425	3.879
31-4	16-2210	4.50	3105	3.778
31-5	17-1035	3.90	3845	3.671
31-6	18-0950	3.10	5240	3.448
		Average		$3.717 \times 10^{-3} \pm 4.6\%$

Procedure: This run was made in the same manner as Run 27, that is, at 25.3° C. except that only 10 milliliter samples were extracted during the run.

No Volhard determination of the chloride ion concentration was run as the value obtained from Run 13 was considered to be accurate enough for use at this temperature also.

Table XXXIV: Run 32-Kinetic Run of the Basic Hydrolysis of $CHCl_3$ in 66 2/3 % Aqueous Dioxane.

Weight flask dioxane $CHCl_3$.....34.7734
Weight flask dioxane.....33.3527
Weight $CHCl_3$..... 1.4207

Initial $CHCl_3$ concentration.....0.02380 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	$k_1 \times 10^3$ ($min.^{-1} g.mol.^{-1} l.$)
32-1	20-1207	(3.93)	0	
32-2	1700	7.32	294	3.659
32-3	21-0830	5.56	1236	4.102
32-4	2206	4.70	2040	3.773
32-5	22-0755	4.08	2631	3.792
32-6	1800	3.60	3234	3.733
32-7	24-1115	2.30	5709	3.501
		Average		3.745±3.7%

Procedure: This run was made at 25.3° C. and in exactly the same way as Run 31. The first point was taken as soon as possible after the addition of the chloroform to see if the chloroform had decomposed, but no acidity was observed.

Table XXXV: Run 33- Kinetic Run of the Basic Hydrolysis of $CHCl_3$ in 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHCl_3$.....34.4813
Weight flask dioxane.....33.0335
Weight $CHCl_3$..... 1.4478

Initial $CHCl_3$ concentration.....0.02425 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	k X 10^2 ($min.^{-1}g.mol.^{-1}l.$)
33-0	20-1501	(4.25)	0	
33-1	1511	7.39	10	11.94
33-2	1521	6.69	20	12.84
33-3	1536	5.87	35	12.72
33-4	1556	4.95	55	12.78
33-5	1621	4.05	80	12.04
33-6	1653	3.27	112	12.30
33-7	21-0843	0.32	1062	
		Average		12.44 X 10^{-2} ±2.7%

Procedure: This run was made in the same manner as Run 30 at 49.9° C. except that 10 milliliter samples were extracted to follow the reaction instead of 12 milliliter samples.

Table XXXVI: Run 34- Kinetic Run of the Basic Hydrolysis of $CHCl_2Br$ in 66 2/3% Aqueous Dioxane

Weight flask	dioxane $CHCl_2Br$.....	40.6120
Weight flask	dioxane.....	38.5903
	Weight $CHCl_2Br$.....	2.0217

Initial $CHCl_2Br$ concentration..... 0.02468 N

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (Minutes)	k X 10^2 ($min.^{-1}g.mol.^{-1}l.$)
34-0	24-1848	(4.27)	0	
34-1	1858	7.53	10	9.860
34-2	1914	6.66	26	10.370
34-3	1941	5.67	53	9.472
34-4	2018	4.44	90	9.746
34-5	2058	3.75	130	8.914

Average 9.672 ± 3.8%

Procedure: The procedure was the same as Run 29 except that 10 milliliters samples were extracted instead of 12 milliliters samples.

Table XXXVII: Run 35- Kinetic Run of the Basic Hydrolysis of $CHCl_2Br$ in 66 2/3% Aqueous Dioxane.

Initial $CHCl_2Br$ concentration.....0.02468 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	$k \times 10^2$ ($min.^{-1}$ $g.mol.^{-1}$ l.)
35-0	24-1855	(4.24)	0	
35-1	1905	7.50	10	9.480
35-2	1920	6.72	25	9.865
35-3	1945	5.65	50	9.930
35-4	2025	4.46	90	9.543
35-5	2105	3.76	130	8.707
		Average		9.505±3.3%

Procedure: This run was the same as Run 34. The same concentration of $CHCl_2Br$ was used since both dioxane $CHCl_2Br$ samples were extracted from the solution made up for Run 34.

Table XXXVIII: Run 36- Kinetic Run of the Basic Hydrolysis of $CHBr_3$ in 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHBr_3$.....32.9826
Weight flask dioxane.....30.1186
Weight $CHBr_3$..... 2.7640

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	$k_1 \times 10^2$ ($min.^{-1} g.mol.^{-1} l.$)
36-0	9-0016	(3.90)	0	
36-1	0017	6.91	1	
36-2	0027	6.09	11	18.29[a]
36-3	0051	5.61	35	9.021
36-4	0141	4.22	85	9.005
36-5	0210	3.65	114	9.825
36-6	0302	2.72	166	9.158
		Average		9.002±1%

[a] Not averaged

Procedure: The same procedure as Run 16 was followed, except that a normal volumetric flask was used and nitrogen was passed into the top each time a point was taken. The bromoform was refractionated before use. The first point was taken as soon after the addition of the bromoform as was possible and the hydroxide ion concentration at this point was taken as the initial concentration to compensate for the acidity of the bromoform added.

A correction was applied to reduce the bromoform concentration by the procedure of considering one bromoform oxidized for each three hydroxide ions used up. This reduced the initial bromoform concentration to 0.02181 M.

Table XXXIX: Run 37- Kinetic Run of the Hydrolysis of $CHBr_3$ in Basic 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHBr_3$.....40.6507
Weight flask dioxane.....37.8508
Weight $CHBr_3$..... 2.7999

Initial $CHBr_3$ concentration.....0.02215 M

Point	Time Samples Extracted	Milliliters 0.0276 N HCl	Time (minutes)	k_1 X 10 ($min.^{-1}$ $g.mol.^{-1}$ l.)
37-0	7-2221	(3.96)	0	
37-1	2227	5.38	6	4.424
37-2	2233	4.31	12	5.051
37-3	2241	3.38	20	4.832
37-4	2251	2.71	30	4.578
37-5	2306	1.95	45	4.366
37-6				
		Average		4.7

Procedure: This run was conducted in the same manner as Run 19 except that it was run at 49.9° C. A sample of the bromoform-dioxane solution was titrated with 0.0506 N sodium hydroxide to determine how much bromoform has oxidized. A 5 ml. sample required 6.75 ml. of sodium hydroxide. This correction reduced the hydroxide ion concentration to 0.0227 N and the initial bromoform concentration to 0.0219 M. The values of the rate constant calculated from these initial concentrations were still unsatisfactory.

Table XLI: Run 38- Kinetic Run of the Basic Hydrolysis of $CHBr_3$ in 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHBr_3$.....32.9418
Weight flask dioxane.....30.1212
Weight $CHBr_3$..... 2.8206

Initial $CHBr_3$ concentration.....0.02232 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	k_1 X 10 ($min.^{-1}$ $g.mol.^{-1}$ l.)
38-0	8-1407	(3.90)	0	
38-1	1408	6.23	1	
38-2	1412	5.37	5	5.325
38-3	1416	4.55	9	5.746
38-4	1427	3.21	20	5.339
38-5	1437	2.57	30	4.789
38-6	1452	1.20	45	6.267
		Average		$5.30 \times 10^{-1} \pm 4.6\%$

Procedure: The same procedure was followed as Run 37. A sample of the bromoform-dioxane solution that was added was titrated against sodium hydroxide to determine the amount of oxidation. A 5 ml. sample required 3.30 ml. of 0.0506 N sodium hydroxide. The initial bromoform concentration was corrected as before to 0.0222 M. Using these values for the initial concentrations, the rate constants were calculated but were not constant throughout the run. They were calculated again using point 38-1 as the initial point. It seemed that there was some acidic impurity in the bromoform that was not separated from the bromoform upon fractionation.

Table XLII: Run 39- Kinetic Run of the Basic Hydrolysis of $CHBr_3$ in 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHBr_3$..... 33.7042
Weight flask dioxane..... 30.9312
Weight $CHBr_3$..... 2.7730

Initial $CHBr_3$ concentration..... 0.02194 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	$k \times 10^2$ ($min.^{-1}$ $g.mol.^{-1}$ l.)
39-0	15-2302	(4.24)	0	
39-1	2303	7.26	1	
39-2	2311	6.85	9	
39-3	2327	6.20	25	9.541
39-4	2352	5.37	50	9.308
39-5	2433	4.12	91	10.11
39-6	16-0100	3.71	118	9.323
39-7	0110	3.57	128	9.124
39-8	0130	3.15	148	9.466
			Average	9.352 ± 1.3%

Procedure: The procedure of Run 36 was reproduced except that the bromoform was repurified by refractionation and fractional crystallization. The values of the rate constants were very satisfactory and agreed with Run 36. Point 39-2 was considered as the initial point for calculations and the bromoform concentrations were corrected accordingly. Point 39-5 was neglected as there was obviously some experimental error.

Table XLIII: Run 40- Kinetic Run of the Basic Hydrolysis of $CHClBr_2$ in 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHClBr_2$..... 33.3895
Weight flask dioxane..... 31.0209
Weight $CHClBr_2$..... 2.3686

Initial $CHClBr_2$ concentrations..... 0.02274 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	$k \times 10^2$ ($min.^{-1} g.mol.^{-1} l.$)
40-0	11-1940	(4.37)	0	
40-1	1941	8.30	1	
40-2	1950	8.03	10	4.825
40-3	2005	7.83	25	4.769
40-4	2034	6.95	54	5.001
40-5	2124	6.07	104	4.693
40-6	2213	5.80	153	3.687*
40-7	2245	5.35	185	3.796
40-8	2325	4.20	225	5.055

*Not averaged Average 4.869 ± 2.6%

Procedure: The same procedure was followed as Run 27. The value of the average rate constant was consistant with that obtained from Run 28. However, two points 40-6 and 40-7 were ignored in taking the average as they were so different. It was decided to duplicated the run taking care to check the run carefully at the two times corresponding to these two points.

Table XLV: Run 41- Kinetic Run of the Basic Hydrolysis of $CHClBr_2$ in 66 2/3% Aqueous Dioxane

Point	Time Sample Extracted	Milliliters 0.0276 N HCL	Time (minutes)	$k \times 10^2$ ($min.^{-1} g.mol.^{-1} l.$)
41-0	12-1345	(4.21)	0	
41-1	1346	7.23	1	
41-2	1356	6.83	11	
41-3	1412	6.48	27	4.914
41-4	1438	6.00	53	4.722
41-5	1538	5.05	113	4.659
41-6	1845	3.25	300	4.331

Procedure: This run was a check on Run 40 and the same procedure and haloform concentrations was used. Since points 41-0 and 41-1 differed so much in the hydroxide ion concentration, even though the time interval was only one minute, the acidity of the chlorodibromomethane dioxane solution that had been added was determined. A 5 ml. sample required 2.40 ml. of 0.0506 N NaOH. The initial $CHClBr_2$ concentration was corrected for the oxidation by considering that each mole of acid formed used up one-third of a mole of haloform. The calculations were made considering point 41-1 as the beginning of the run. The values, though, were not constant but decreased in value as the run proceeded. The rate constants were calculated again, using point 41-2 as the initial point. The $CHClBr_2$ concentration had to be corrected for the amount that had been used up. This gave a value of 0.0222 M. These are the values tabulated for the run.

Table XLVI: Run 42- Kinetic Run of the Basic Hydrolysis of $CHClBr_2$ in 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHClBr_2$..... 33.0085
Weight flask dioxane..... 30.6176
Weight $CHClBr_2$..... 2.3909

Initial $CHClBr_2$ concentration..... 0.02295 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	($Min.^{-1}g.mol.^{-1}l.$)
42-0	12-2115	(4.27)	0	
42-1	2116	8.08	1	
42-2	2126	7.80	11	5.200
42-3	2140	7.46	25	4.938
42-4	2205	6.90	50	4.867
42-5	2255	5.90	100	4.301
42-6	2345	5.10	150	4.929
42-7	13-0020	4.75	185	4.648

Average 4.814 ± 4.7%

Procedure: This run was made following the same procedure as Run 41. This run had the first point, taken only one minute after the start of the run, which showed a decrease in hydroxide ion concentration, so it, instead of point 42-0, was used as the initial point. The values thus calculated were satisfactory and checking the run at times corresponding to those in Run 40 showed no repetition of the inconsistency.

Table XLVII: Run 43- Kinetic Run of the Basic Hydrolysis of $CHBr_3$ in 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHBr_3$..... 34.1196
Weight flask dioxane..... 31.3012
Weight $CHBr_3$..... 2.8184

Initial $CHBr_3$ concentration..... 0.02159 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	$k \times 10^2$ ($min.^{-1} g.mol.^{-1} l.$)
43-0	16-0238	(4.24)	0	
43-1	0239	7.50	1	
43-2	0245	7.41	7	
43-3	0301	7.25	23	1.991
43-4	0325	7.03	47	1.915
43-5	0440	6.43	122	1.808
43-6	0603	5.72	205	1.964
43-7	1040	3.82	482	1.763
			Average	1.888 ± 4%

Procedure: This followed the procedure of Run 39 except that it was run at 25.3°C. The rate constants were calculated using point 43-2 as the initial hydroxide ion concentration. The corrected bromoform concentration was 0.02159 M.

Table XLVIII: Run 44- Kinetic Run of the Basic Hydrolysis of $CHBr_3$ in 66 2/3% Aqueous Dioxane.

Initial $CHBr_3$ concentration..... 0.02230 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	$-\frac{1}{2}k \times 10^2$ (min.$^{-1}$ g.mol.$^{-1}$ l.)
44-0	16-0340	(4.16)	0	
44-1	0342	7.24	2	
44-2	0357	7.06	17	
44-3	0423	6.80	43	2.063
44-4	0453	6.58	73	1.856
44-5	0558	6.02	178	1.951
44-6	1050	4.05	426	1.951
			Average	1.955 ± 2.7%

Procedure: The same procedure as Run 43 was followed. The bromoform sample was obtained from the same dilution. Point 44-2 was considered as the initial point for the calculation of the rate constant. The corrected bromoform concentration was 0.02138 M.

Table XLIX: Run 45- Kinetic Run of the Basic Hydrolysis of $CHBr_3$ in 66 2/3% Aqueous Dioxane.

Weight flask dioxane $CHBr_3$..... 35.8892
Weight flask dioxane..... 33.0840
Weight $CHBr_3$..... 2.8052

Initial $CHBr_3$ concentration..... 0.0210 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCL	Time (minutes)	$k \times 10^1$ ($min.^{-1} g.mol.^{-1} l.$)
45-0	23-1330	(4.10)	0	
45-1	1331	6.70	1	
45-2	1335	5.75	5	5.790*
45-3	1340	4.98	10	5.094
45-4	1350	3.64	20	5.202
45-5	1400	2.73	30	5.196
45-6	1409	2.12	39	5.094

* Not Averaged Average 5.147 ± 1%

Procedure: This run was made following the same procedure as Run 38, except that the bromoform was purified by both fractional distillation and fractional crystallization. In the calculations, point 45-1 was used as the initial point and the bromoform concentration corrected as before to account for this change. The corrected value was 0.0210 M.

Table L: Run 47- Reaction of Sodium p-Thiocresolate with Chloroform in 66 2/3% Aqueous Dioxane.

Time Extracted	Time (minutes)	Milliliters 0.0608 N I_2	% reacted
28-0016	0	12.50	
1730	1034	9.90	21

Procedure: The procedure is discussed under Reaction of Sodium p-thiocresolate with the Haloforms.

Table LI: Run 48- Reaction of Sodium p-Thiocresolate with Chloroform in 66 2/3% Aqueous Dioxane

Time Extracted	Time (minutes)	Milliliters 0.0608 N I_2	% reacted
28-0314	0	21.70	
2015	1021	21.65	.23

Procedure: This run was the run corresponding to Run 47, except that there was no excess hydroxide present. The proportions of reagents were different but the rest of the procedure was exactly the same. The time differences between the initial and final points was also the same. The proportions of reagents were 10 ml. of 1.026 N NaOH, 15 ml. of distilled water, 70 ml. of purified dioxane and 2 grams of p-thiocresol.

Table LII: Run 49- Reaction of Sodium p-Thiocresolate with $CHBr_3$ in 66 2/3% Aqueous Dioxane.

Time Extracted	Time (minutes)	Milliliters 0.0608. N I_2	% reacted
28-0235	0	17.60	
0436	120	15.50	11.9

Procedure: This run was exactly the same as Run 47.

Table LIII: Run 50- Reaction of Sodium p-Thiocresolate with $CHCl_2Br$ in 66 2/3% Aqueous Dioxane.

Time Extracted	Time (minutes)	Milliliters 0.0608 N I_2	% reacted
28-0043	0	15.20	exploded
0225	0	22.80	
0325	60	20.30	11.1

Procedure: This run was made following the same procedure as Run 47.

Table LIV: Run 51- Reaction of Sodium p-Thiocresolate with $CHClBr_2$ in 66 2/3% Aqueous Dioxane.

Time Extracted	Time (minutes)	Milliliters 0.0608 N I_2	% reacted
28-0045	0	19.40	
0345	180	16.30	16.0

Procedure: The procedure of Run 47 was followed.

Table LV: Run 52- Reaction of Sodium p-Thiocresolate with $CHBr_3$ in 66 2/3% Aqueous Dioxane.

Time Extracted	Time (minutes)	Milliliters 0.0608 N I_2	% reacted
28-0250	0	22.20	
0450	120	21.34	3.14

Procedure: This run corresponded to Run 48 for Chloroform in which no excess hydroxide ion was present. The same procedure was followed except that bromoform was used instead of chloroform.

Table LVI: Run 53- Reaction of Sodium p-Thiocresolate with $CHCl_2Br$ in 66 2/3% Aqueous Dioxane.

Time Extracted	Time (minutes)	Milliliters 0.0608 N I_2	% reacted
28-0315	0	21.90	
0415	60	20.52	2.5

Procedure: The procedure of Run 48 was followed.

Table LVII: Run 54- Reaction of Sodium p-Thiocresolate with $CHClBr_2$ in 66 2/3% Aqueous Dioxane.

Time Extracted	Time (minutes)	Milliliters 0.0608 N I_2	% reacted
28-0250	0	21.45	
0550	180	19.90	7.25

Procedure: The procedure of Run 48 was followed.

TABLE LVIII: Run 55- Reaction of Sodium p-Thiocresolate with $CHBr_3$ in 66 2/3% Aqueous Dioxane.

Time Extracted	Time (minutes)	Milliliters 0.0608 N I_2	% reacted
23-1500	0	24.00	
1700	120	20.00	16.7

Procedure: This run was made in the same manner as Run 49 except that the proportions of reagents were changed to give a larger excess of hydroxide ion. The initial hydroxide ion concentration was about 0.09 N. The amount of reagents used were 25 ml. of 1.026 N sodium hydroxide, 10 ml. of distilled water, 70 ml. dioxane and 2 grams of p-thiocresol.

Table LIX: Run 56- Reaction of Sodium p-Thiocresolate with $CHBr_2Cl$ in 66 2/3% Aqueous Dioxane.

Time Extracted	Time (minutes)	Milliliters 0.0608 N I_2	% reacted
23-1503	0	23.10	
1558	50	17.50	24.2

Procedure: This run followed the procedure of Run 55.

Table LX: Run 57- Reaction of Sodium p-Thiocresolate with $CHBr_2Cl$ in 66 2/3% Aqueous Dioxane.

Time Extracted	Time (minutes)	Milliliters 0.0608 N I_2	% reacted
23-1505	0	23.80	
1600	55	22.50	5.5

Procedure: This run was a check of Run 54 and followed it.

Table LXI: Run 58- Reaction of Sodium p-Thiocresolate with $CHBrCl_2$ in 66 2/3% Aqueous Dioxane.

Time Extracted	Time (minutes)	Milliliters 0.0608 N I_2	% reacted
23-1507	0	24.00	
1537	30	18.50	23.0

Procedure: The procedure followed for this run was the same as Run 55.

Table LXII: Run 59- Reaction of Sodium p-Thiocresolate with $CHCl_2Br$ in 66 2/3% Aqueous Dioxane.

Time Extracted	Time (minutes)	Milliliters 0.0608 N I_2	% reacted.
23-1508	0	24.10	
1538	30	22.60	6.1

Procedure: This run was exactly the same as Run 48.

Table LXIII: Run 60- Kinetic Run of the Basic Hydrolysis of CHClBrF in 66 2/3% Aqueous Dioxane.

Weight of bottle dioxane CHClBrF.....		46.2492
Weight of bottle dioxane.....		45.7242
	Weight of CHClBrF.....	0.5250

Initial CHClBrF concentration..... 0.00712 M

Point	Time Sample Extracted	Milliliters 0.0276 N HCl	Time (minutes)	k ($min.^{-1} g.mol.^{-1} l.$)
60-0	30-1315	(4.80)	0	
60-1	1316	(4.34)	1	
60-2	1321	7.90	6	.914
60-3	1330	6.90	15	.823
60-4	1345	5.80	30	.724
60-5	1420	4.40	65	.576
60-6	1540	2.90	145	.439

Average .695±18.7%

Procedure: This run followed the same procedure as Run 12 with the following exceptions: (1) The temperature of the constant temperature bath was 0° C., which was accomplished by filling a large container with an ice-water mixture and keeping it well agitated with a stirrer. (2) The pipettes were kept in the refrigerator at about 0° C., until used, to keep the temperature as low as possible. (3) Only one-fifth of a ml. of CHClBrF was added to the 25 ml. volumetric flask and diluted to the mark. (4) The sodium hydroxide concentration was reduced by adding 3 ml. of approximately 0.30 N NaOH. (5) The titration for the hydroxide ion was done with 0.01 N HCl.

Table LXIV: Run 61- Kinetic Run of the Basic Hydrolysis of CHFClBr in 66 2/3% Aqueous Dioxane.

Point	Time Sample Extracted	Milliliters 0.0276 N HCL	Time (minutes)	K($min.^{-1}g.mol.^{-1}l.$)
61-0	30-1410	(4.80)	0	
61-1	1411	8.85	1	
61-2	1415	7.95	5	1.291*
61-3	1425	6.95	15	.859
61-4	1440	5.85	30	.733
61-5	1535	3.80	85	.551

* Not Averaged Average .816 ± 26.5%

Procedure: The same procedure as Run 60.